Electrochemical Generation of Optically Active Iminium Ion

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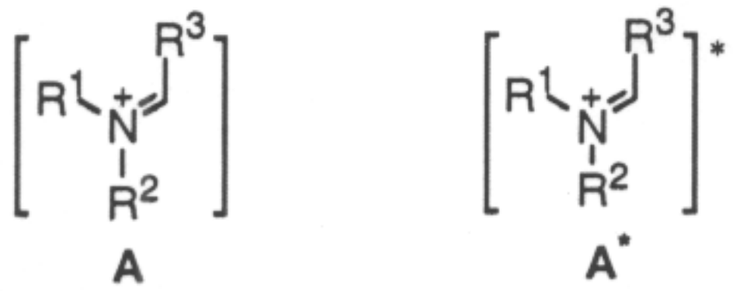
Iminium ions **A** are typical carbenium ions stabilized by the adjacent nitrogen atom.



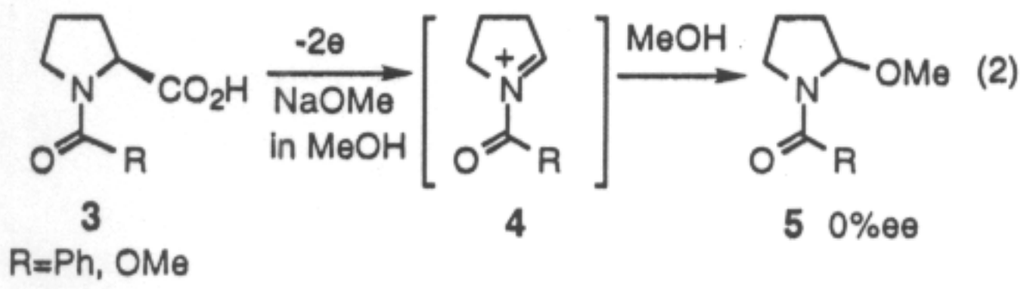
A **A***

Thus, memory of chirality through iminium ions as intermediates has been recognized much difficult. Recently, however, we found a first memory of chirality through acyliminium ions **B** which are generated by electrochemical oxidation of *N*-acyl-α-amino acids **1** (eq 1).[1] We report herein further development of this finding as well as the application to the generation of optically active iminium ions **A***.

1 **B** **2** (1)

1) Memory of chirality through intermediates **B**

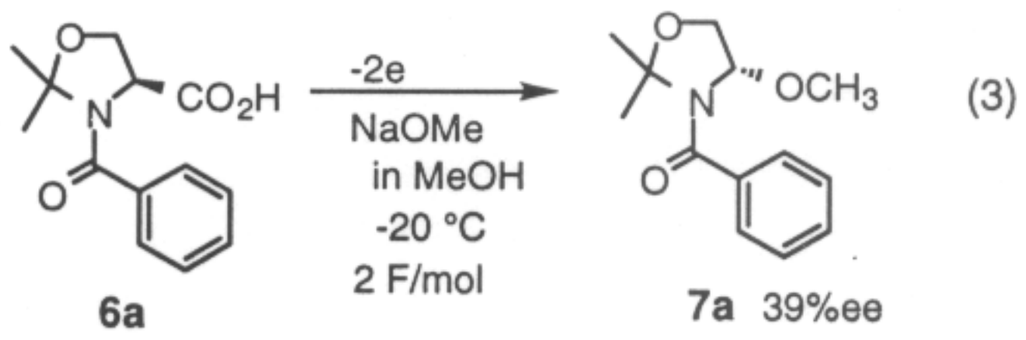
The non-Kolbe reaction of optically active *N*-acyl-α-amino acids **3** in methanol affords *N,O*-acetals **5**, in which the original chirality of **1** is completely lost because of an intervention of acyliminium ions **4** as intermediates (eq. 2).



3 R=Ph, OMe **4** **5** 0%ee (2)

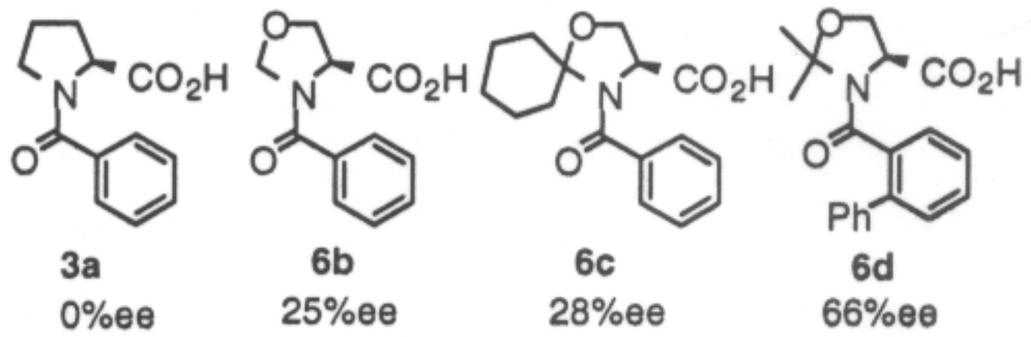
On the other hand, we found that the non-Kolbe electrolysis of **6** derived from L-serine gave the corresponding *N,O*-acetal **7** in 39%ee (eq. 3).[1]

In order to improve the ee in the oxidation, we surveyed a variety of modified compounds **6b-d**. [2]



6a **7a** 39%ee (3)

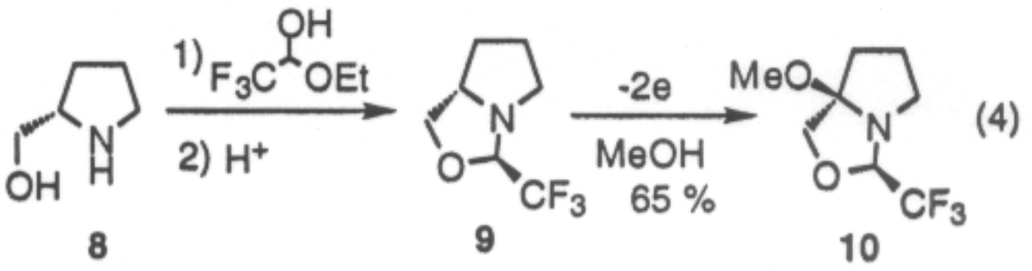
The result is as follows.



3a 0%ee **6b** 25%ee **6c** 28%ee **6d** 66%ee

2) Memory of chirality through intermediates **A*** [3]

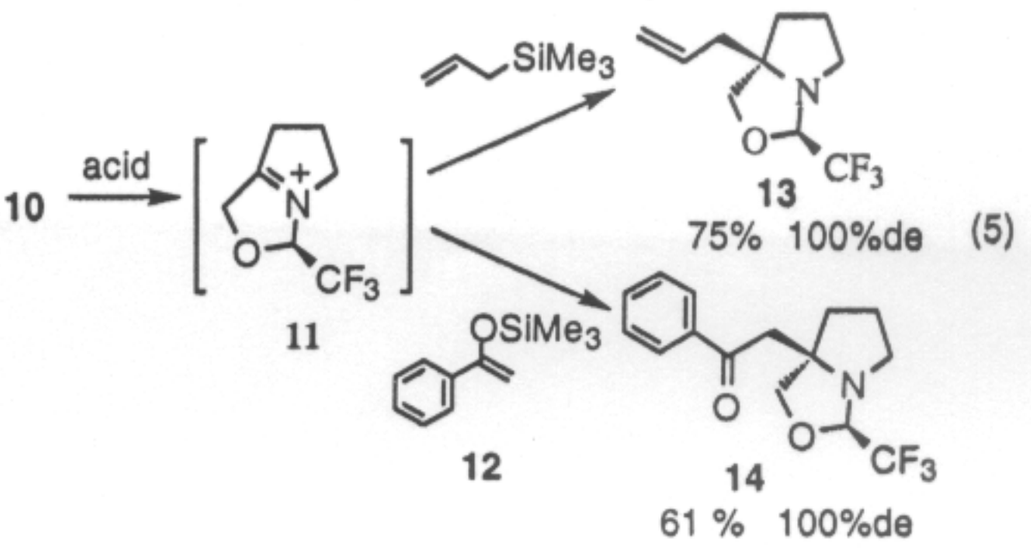
N,O-acetal **10**, a precursor of iminium ion, was prepared by electrochemical oxidation of **9**, which was derived from optically active amino alcohol **8** (eq 4).



8 **9** **10** (4)

The oxidation potential (Ep) of **9** was 1.91 V vs Ag/AgCl. The value was largely positive than that of **8** (1.24 V), and more negative than that of *N*-methoxycarbonylpyrrolidine (2.17 V).

Treatment of **10** with CF_3CO_2H in CH_2Cl_2 gave iminium ion **11**, which could be trapped with carbon nucleophiles such as allyltrimethylsilane and silyl enol ether **12** to give the products **13** and **14**, respectively, with complete diastereoselectivity (100%de) (eq 5).



11 **12** **13** 75% 100%de **14** 61 % 100%de (5)

Iminium ion **11** was enough stable at rt to allow the measurement of its ^1H NMR spectrum; δ ($CDCl_3$) 6.35 for CF_3CH, 5.60 for OCH_2.

References

1. Matsumura, Y.; Shirakawa, Y.; Satoh, Y.; Umino, M.; Tanaka, T.; Maki, T.; Onomura, O. *Org. Lett.* **2** (2000) 1689.
2. A part; Matsumura, Y.; Tanaka,T.; Wanyoike, G. N.;Maki, T.; Onomura, O. *J. Electroanal. Chem.*, in press (2001).
3. unpublished.